

Hot Gas Desulfurization Using Moving-Bed Reactor

Raúl E. Ayala (Raul.Ayala@crd.ge.com; 518-387-5850)
Venkat S. Venkataramani (venkata@crd.ge.com; 518-387-5322)
Timothy L. Chuck (chucktl@crd.ge.com; 518-387-6523)
GE Corporate Research and Development
One Research Circle,
Schenectady, NY 12309

Introduction

Coal gas desulfurization at elevated temperatures is now recognized as crucial for efficient and economic coal utilization in Integrated Gasification Combined-Cycle (IGCC) systems. Recent system studies of IGCC technology have suggested the temperature range of 350 °C to 550 °C (662 °F to 1022 °F), instead of temperatures above 1200 °F (648 °C), as a desirable range to remove coal gas contaminants, particularly sulfur species [Droog et al., 1993; Schreurs, 1994]. In general, the benefit to be gained at these “lower” temperatures (e.g., lower plant costs, hardware reliability, and engineering feasibility) outweighs the slight loss in desulfurization efficiency and still result in a lower overall cost of electricity. The U.S. Department of Energy/Federal Energy Technology Center (DOE/FETC) has sponsored development of various configurations of high-temperature desulfurization systems using mixed metal oxide sorbents over the last decade [McDaniel et al., 1995], and a need exists for the development of more efficient sorbents for this temperature range.

GE is developing a moving-bed, high-temperature desulfurization system for integrated gasification combined-cycle (IGCC) power systems in which zinc-based regenerable sorbents are currently being used as desulfurization sorbents [Ayala et al., 1996; Furman et al., 1996]. Zinc titanate and other zinc-based oxides are being considered as sorbents for use in the Clean Coal Technology Demonstration Program at Tampa Electric Co.’s (TECo) Polk Power Station I. A key to success in the development of high-temperature desulfurization systems is the matching of sorbent properties, (i.e., sustainable desulfurization kinetics, sulfur capacity, and mechanical durability over multiple cycles) to operate at the design plant operating conditions. Integrating desulfurization with gasifier and turbine components in the IGCC system results in a more efficient overall system [Rath et al., 1994; Buchanan et al., 1994; Corman, 1986].

Objectives

In this program, the effort is geared towards developing advanced mixed-metal oxide sorbents for desulfurization in moving-bed systems in the temperature range 343-538 °C (650-1000 °F), where technical viability and process efficiency result in lower overall process costs. In addition,

Research sponsored by the U.S. Department of Energy’s Morgantown Energy Technology Center, under contract DE-AC21-94MC31089, “Advanced Sorbent Development Program,” with GE Corporate Research and Development, One Research Circle, Schenectady, NY 12309; telefax: 518-387-7258

a cost assessment and a market plan for large-scale fabrication of sorbents will be developed. As an optional task, a long-term bench-scale testing of the best moving-bed sorbent formulation will be conducted.

The near-term thrust of moving-bed sorbent development is to support the commercialization of the GE hot gas cleanup demonstration system at Tampa Electric Co.'s Polk Station I, where desulfurization will take place near 430-500 °C (~800-930 °F). The long-term thrust is to develop moving-bed sorbents for use in future IGCC systems optimized to operate at temperatures from 538 °C (1000 °F) to as low as 343 °C (650 °F).

Project Description

This project is being pursued as part of DOE/FETC Program "Advanced Sorbent Development" which includes development of sorbents for both moving-bed and fluidized-bed applications. GE Corporate Research and Development (GE-CRD) is acting as the main contractor to DOE and is also in charge of the development of moving-bed sorbents described in this paper. The Institute of Gas Technology (IGT) is acting as a subcontractor to GE-CRD in the development of sorbents for fluidized-bed applications. IGT's work is presented under a separate paper at this conference [Abbasian 1997].

Three classes of sorbent materials are being considered for moving-beds: zinc-based materials (particularly zinc titanates), advanced (non-zinc) metal oxide materials, and proprietary materials developed by independent vendors. Work at GE on zinc titanate sorbent materials has been published under previous DOE contracts [Ayala et al., 1996; 1995a, 1995b, 1994]. A review study of non-zinc metal oxides suitable for desulfurization in the 343-538 °C range was performed and reported in the literature [Ayala et al., 1995b].

The implementation of hot coal gas desulfurization heavily relies on the development of regenerable sorbent materials that have high sulfur capacity and can efficiently remove H₂S (from several thousand ppmv levels down to a few ppmv) over many cycles of sulfidation/regeneration. Structural stability and good mechanical strength are also desirable features in a sorbent. Not surprisingly, only a few metal oxides can meet these stringent requirements.

Results

The effort in this project has concentrated in two aspects during the past year:

1. Screening of proprietary sorbents for potential use in pilot-scale systems, and
2. Modification of zinc titanate sorbents for added mechanical strength during multiple-cycle testing and added reactivity during operation at lower temperatures from 482 °C (900 °F) down to 343 °C (650 °F) .

This paper will present only a summary of the proprietary sorbents and will concentrate on the fabrication and evaluation of modified zinc titanate sorbents.

Screening of proprietary sorbents

Two proprietary sorbents were evaluated in laboratory tests at GE's facilities during 1996: the manganese-based sorbents developed by Chemetals' Inc., and the ICCI-2 sorbent developed by the Illinois Clean Coal Institute and E&A Associates. Chemetals Inc. (Baltimore, MD) provided several formulations of manganese-based sorbents for evaluation. Some of the formulations were tailored to achieve low equilibrium H_2S comparable to zinc-based sorbents by compositional modifications. The results obtained in GE's laboratory tests yielded satisfactory desulfurization performance, but more testing is needed to fully understand the regeneration characteristics and compatibility of these sorbents with the current GE moving-bed system at TECo. More details are given the GE 1996 Annual Technical Report [Ayala et al., 1997].

Bench testing of the Illinois Clean Coal Institute's ICCI-2C formulation, as provided by Dr. J. Swisher of Southern Illinois University (SIU)/E&A Associates, was performed at GE during the latter part of 1996. The purpose of the screening was to determine the compatibility of the ICCI-2C with the GE pilot plant operating conditions. From results obtained in the tests, it was concluded that the ICCI-2 sorbent was acceptable for consideration in future pilot plant testing. No testing was done at GE-CRD to assess operability at TECo conditions (where regeneration will be performed at a pressure of 5 to 7 atm, versus 1.5 atm as in GE's HGCU pilot plant). A summary of the results was submitted to E&A Associates and to DOE/FETC. More details of the testing are provided in this program's 1996 Annual Technical report [Ayala, 1997] and under a separate paper at this conference [Swisher 97].

The rest of this paper will focus on the development of modified zinc titanates (MZT) for the moving-bed system. Zinc titanate has been under study for several years, and there is a significant amount of information on its performance characteristics in reducing (coal) and oxidizing (regeneration) gases. With respect to desulfurization ability, its performance has been excellent, and there is little doubt on its suitability for use at temperatures below 600 °C [Furman et al. 1996, Bevan et al., 1995]. However, as with any other sorbent, there is always a desire to further minimize overall HGCU operating costs by reducing the sorbent replacement cost via improvements in the sorbent mechanical durability (attrition resistance and crush strength).

Screening of modified zinc titanate powders

Currently, modification of zinc titanate sorbents is being pursued at GE-CRD and United Catalysts, Inc. (UCI, Louisville, Kentucky) in support of TECo's hot gas cleanup demonstration plant. The two major objectives in mind are:

1. to increase the mechanical strength of zinc titanate (Zn_2TiO_4) sorbent pellets, by addition of phase-stability modifiers and modification of pelletization procedures.

2. to increase the lower limit of operation during desulfurization below 482 °C (900 °F) towards 343 °C (650 °F) (desulfurization-rate additives) by introduction of additives into the zinc titanate structure. The desire for sustained, more robust reactivity at temperatures below 482 °C is to address operation during transient (startup/shutdown) or off-design operation of the gasification and cooling systems in IGCC plants.

Evaluation of the modified zinc titanates (MZT) was first conducted using powder formulations to determine the interrelations between chemical compositions and reaction rates during desulfurization and regeneration. Tests were performed to ascertain that the presence of additives in powders would not have a negative effect on the desulfurization reactivity, sulfur removal capacity, and regenerability of zinc titanate. The second part of the testing involved pelletizing the formulations and assessing the mechanical characteristics (attrition and crush strength) of the fresh and reacted sorbents.

Approximately 30 powder formulations were prepared during 1996 to assess chemical reactivity. Table 1 presents the designation of a few of the powder formulations that were prepared with promising desulfurization and regeneration properties.

Table 1. GE Modified Zinc Titanate Formulations*

Formulation Number	GE Designation	Comment
1	ZT9601	reference plain zinc titanate
2	ZT9602	molybdenum additive
3	ZT9603	desulfurization additive
4	ZT9606	strengthening additive
5	ZT9607	phase stability additive
6	ZT9608	phase stability additive
7	ZT9605	phase stability additive
8	ZT9604	Mo + stabilizing additive

* Preparation methods covered under U.S. Patent 5,188,811 issued 2/23/1993

Formulations 1 and 2 are the standard zinc titanate without additives and zinc titanate with molybdenum additive described in previous work. These two formulations were fabricated again as reference materials to provide a comparison with prior zinc titanate sorbents performance in the GE pilot plant during 1995 (see [Furman et al., 1996; Bevan et al., 1995]). Formulation 3 contains additives to test increase the desulfurization capability in the temperature range 370-482 °C (700-900 °F). Formulation 4 contains an additive for strength.

Chemical reactivity of sorbents was assessed using a thermogravimetric analyzer (TGA). In a TGA test, the weight of a powder or pellet sample hanging from the microbalance is monitored as a function of time. The weight gain is proportional to the extent of reaction in the sample. For pure zinc titanate (Zn_2TiO_4), the complete sulfidation reaction (26% wt/wt sulfur on the sorbent) corresponds to a weight gain of 12.6%. Of course, addition of inerts and binders reduces the weight gain observed at saturation, but reproducibility of the weight changes through multiple

cycles of absorption and regeneration is the key parameter in sorbent development. In a typical TGA reactivity test, the pellets are exposed to simulated clean coal gas (without H_2S) for the first 30 minutes at 1 atm and 482 °C to establish a weight baseline. Then, 3% H_2S is introduced during absorption (also called sulfidation) to check for weight changes during the reaction. A regeneration with 2-4% O_2 can follow the sulfidation when the weight should return to its base value. Repetitive cycles of sulfidation and regeneration can be carried out in a multiple cycle test. A typical example of a TGA powder formulation with a phase stability additive is shown in Figure 1, where two sulfidations are shown. A horizontal baseline is measured in the first 30 minutes of each absorption, and essentially no loss in reactivity is observed between the first and the second absorptions. Standard conditions for TGA sulfidation tests at GE are 3% H_2S in simulated coal gases at 482 °C and 1 atm.

Figure 2 presents the reactivity of ZT9603 zinc titanate. This formulation has desulfurization additives and no phase stabilizers. Some initial loss in capacity is observed, either due to sulfate formation or structure densification.

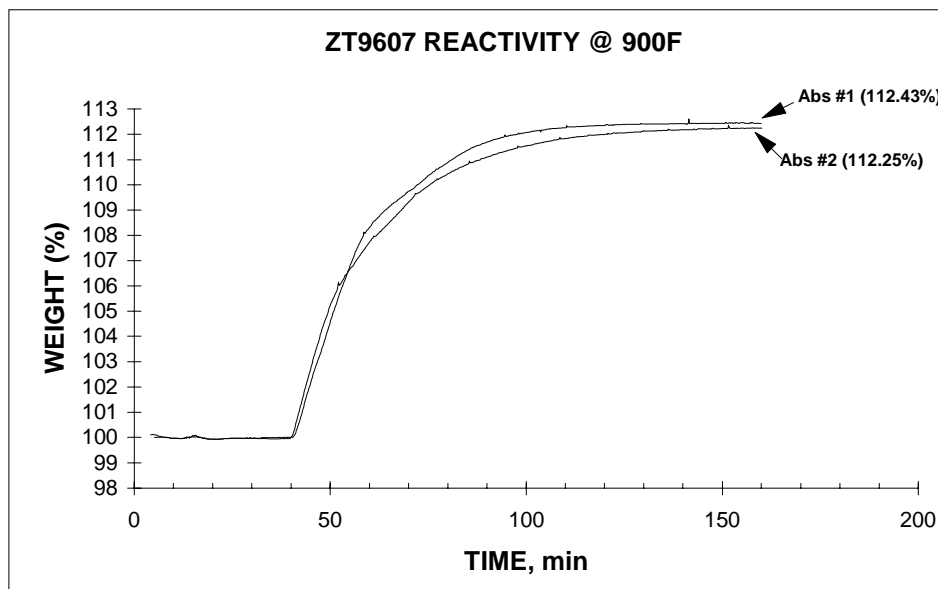


Figure 1. TGA Chemical reactivity of ZT9607 zinc titanate

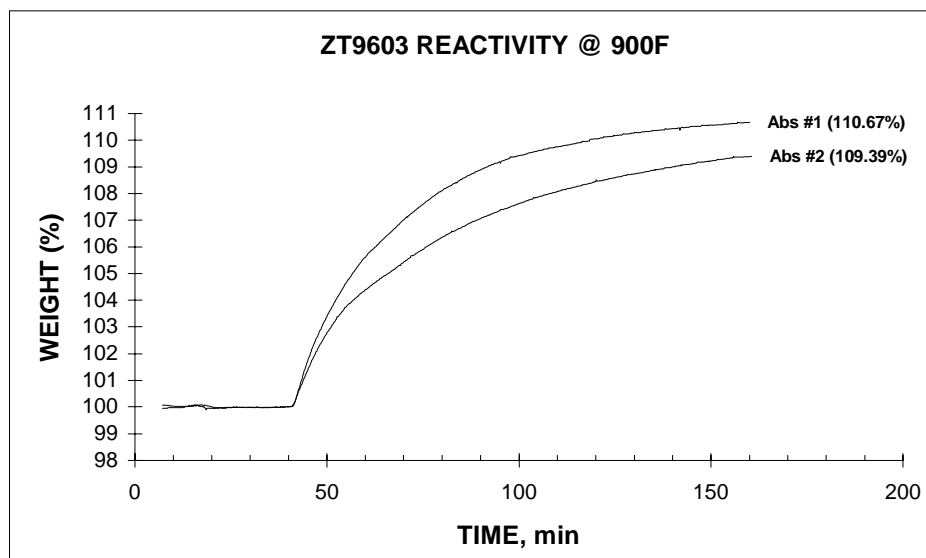


Figure 2. TGA Chemical reactivity of ZT9603 zinc titanate without stabilizer

Figure 3 shows the TGA curves for the first sulfidation of several of the formulations obtained at 482 °C, 1 atm, and 3% H₂S in the simulated coal gas. TGA tests show that the reactivity of the top five formulations is satisfactory, i.e., that the strengthening and desulfurization enhancing additives are not detrimental to the desulfurization and regeneration of the sorbents. The theoretical capacity of the modified zinc titanate powders is between 10% and 12% weight gain, so all the curves exhibit a normal behavior of weight gain to close to saturation after the two hour test. Differences in the total sulfur capacity among the sorbents are a result of differences in the zinc titanate initial concentration in the formulation. Also, none of the formulations lose or gain weight prior to introduction of H₂S (0 to 40 minutes), which indicates a stable crystal structure in the presence of H₂ and CO in the simulated coal gas.

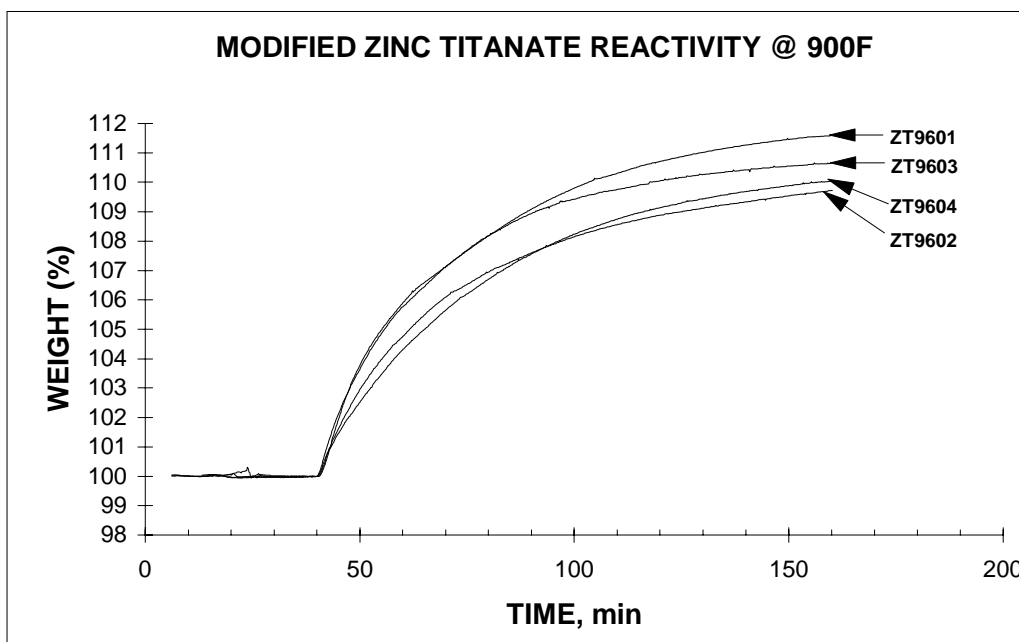


Figure 3. TGA reactivity of modified zinc titanate powders at 1 atm and 492 °C/900 °F

After completion of the reactivity tests on powder formulations, UCI was requested to pelletize these formulations to test their mechanical properties (attrition resistance and crush strength) at GE-CRD.

Screening of pelletized modified zinc titanates

The purpose of the pelletization studies at UCI was to improve the mechanical durability of zinc titanate sorbent formulations by adjusting the pelletization conditions (i.e., time, temperature, pore modifiers, and binders) that would result in an improved overall (chemical and mechanical) performance. Typically, mechanically strong pellets have low reactivities and highly reactive pellets tend to be soft. A balance between both properties is usually necessary to achieve optimum performance.

The following key areas of sorbent performance were considered for comparison among formulations:

- mechanical durability (attrition and crush strength) of fresh and cycled sorbents,
- desulfurization and regeneration characteristics during normal operation,
- sulfate formation tendency during regeneration, and
- temperature range of desulfurization.

All modified zinc titanate formulations were tested as received from UCI. No interim conditioning or activation of the pellets was necessary between the as-received state and the test samples used in this paper.

Mechanical durability of fresh sorbents

Several formulations of modified zinc titanate sorbents were extruded, formed, and calcined by UCI. The resulting pellets had a 3-4 mm diameter. The first round of pelletized zinc titanate formulations was received in January 1997 (Table 2). Crush strength was acceptable (i.e., greater than 3 lb/pellet or 1.36 Kg/pellet) and reactivity was also reasonable (not shown). However, ASTM attrition for most of the fresh formulations was above the target value of less than 4%.

Table 2. Properties of the first round of fresh pelletized samples

Formulation	Crush Strength, lb/pellet (Kg/pellet)	ASTM Attrition, %	Presence of broken granules after ASTM attrition tests
PP-4114	6.5 (2.9)	1.32	No
PP-4115	5.9 (2.7)	10.85	No
PP-4116	5.1 (2.3)	16.15	No
PP-4117	4.6 (2.1)	8.64	Yes
PP-4118	3.9 (1.8)	5.22	Yes

Given that pelletization of modified zinc titanates in the first round fell short of achieving a high mechanical strength (i.e., ASTM attrition less than 4%), preparation of a second round of formulations with the same compositions was undertaken again at UCI. This time, pelletization procedures were tailored to the particular extrusion characteristics of the formulations. The objective for preparation of a second round of formulations was to obtain 2% or less ASTM attrition loss, or half the maximum acceptable for a fresh sorbent.

Table 3 shows the physical properties of the second round of fresh sorbents. The crush strength values are higher than those measured in the first round (Table 2), and well above the minimum of 3 lb/pellet needed to prevent pellet crushing under its own bed weight. ASTM attrition loss values were lower than those in Table 2 and, except for formulation MZT-G1, achieved the internal target of 2%, which is half of the 4% ASTM attrition loss target for evaluation in pilot plant operation.

Table 3. Mechanical properties of the second round of zinc titanate formulations

GE ID	Crush Strength, lb/pellet (Kg/pellet)	ASTM Attrition, %
MZT-P1	8.3 (3.8)	1.0
MZT-R1	4.9 (2.2)	2.0
MZT-G1	4.8 (2.2)	2.5
MZT-I1	6.0 (2.7)	2.0
MZT-O1	5.4 (2.4)	0.9

Desulfurization and regeneration characteristics

TGA chemical reactivity tests were conducted on the pelletized sorbent formulations at GE-CRD. Figure 4 shows the typical weight gain during absorption for the first two cycles of MZT-I1, while Figure 5 shows the corresponding weight gain of MZT-O1. Again, the first 30 minutes correspond to exposure to simulated clean coal gas (without H₂S) to establish a weight baseline. An acceptable weight gain is 5% above the stable initial baseline in the first 2 hours. This weight gain corresponds the operating point for the moving-bed system (i.e., 6.7 lb/ft³ of bed) for these formulations. Both formulations met this requirement. MZT-I1 is slightly more stable than MZT-O1 since the difference in sulfur loading against time for repetitive absorptions is more predictable. The difference in behavior between the two formulations is probably a result of different chemical compositions and preparation method.

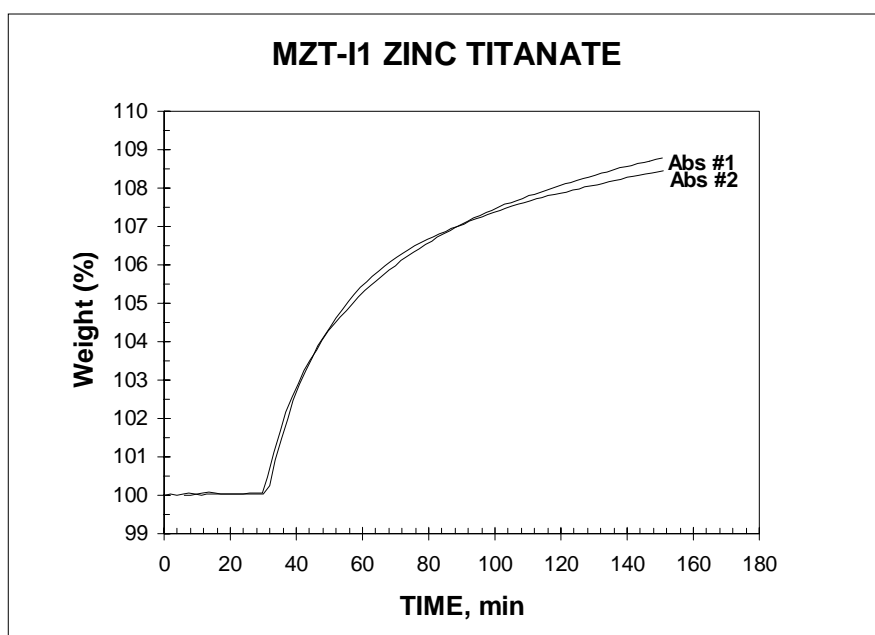


Figure 4. TGA reactivity of (MZT-I1) during sulfidation 1 atm and 492 °C/900 °F.

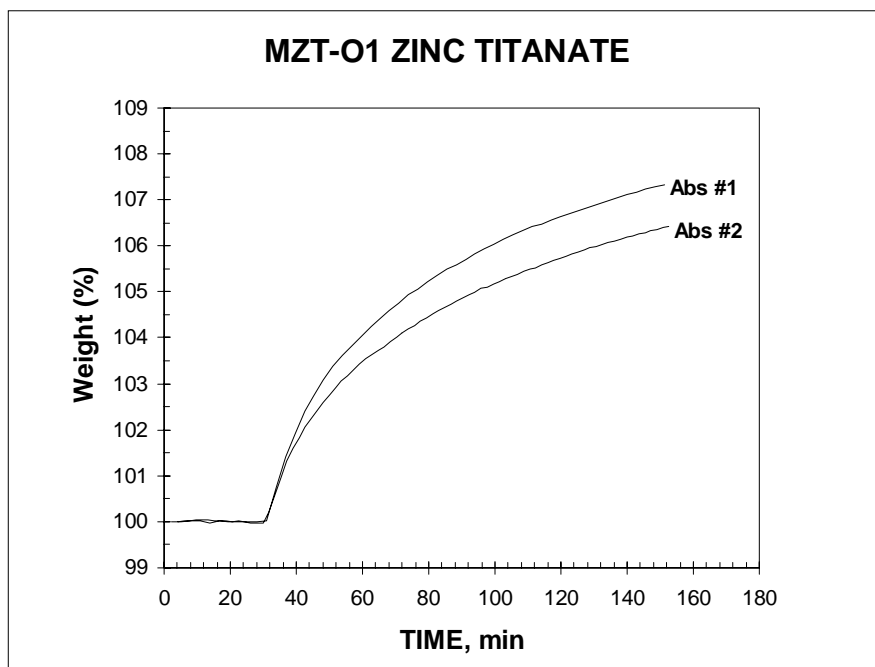


Figure 5. TGA reactivity of MZT-O1 during sulfidation at 1 atm.

Sulfate formation during regeneration

Dry regeneration of zinc-based sorbents with diluted air produces sulfur dioxide which is used as a starting material for sulfuric acid production or elemental sulfur. However, sulfur species may remain in the sorbent as residual solid zinc sulfates. The presence of zinc sulfates is highly undesirable because it reduces the sulfur capacity of the sorbent in subsequent cycles and eventually cannot be removed from the sorbent even with thermal treatment. The TGA weight gain of the sorbent pellets due to sulfate formation is presented in Figure 6. After establishing a baseline steady weight of the sorbent at 718 °C (1325 °F) under nitrogen for twenty minutes, the sorbent was exposed to a gas containing 5% SO₂, 2% O₂ at 718 °C (1325 °F) and 1 atm. Higher weight gains are indicative of detrimental faster rates of sulfate formation for the sorbent in the 2 hour exposure time. Plain zinc titanate (MZT-P1) has the higher sulfate formation tendency while those with additives have a reduced tendency. Lower zinc sulfate formation tendencies are beneficial because they minimize sorbent deterioration.

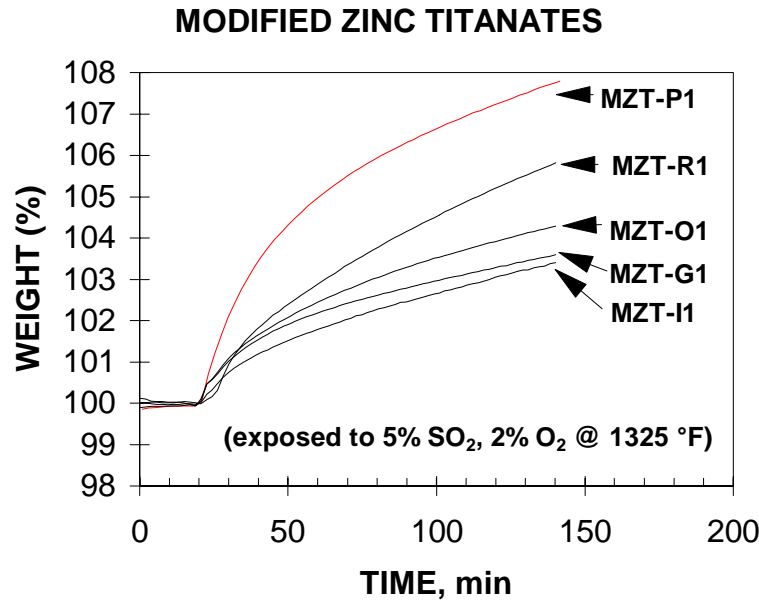


Figure 6. TGA weight gain due to sulfate formation during regeneration of the pelletized modified zinc titanates at 1 atm

Temperature range of desulfurization

In order for a sorbent to be useful in HGCU operation, it has to be able to desulfurize coal gas in reasonable times, i.e., have a chemical reactivity for sulfur species compatible with practical reactor size, not only at steady state but also during transient startup/shutdown operations. Typical startup and shutdown operations for an absorber require operation at lower temperatures (below 482 °C). Off-design operation may also require operation in this temperature window for extended periods of time. Because of these reasons, sulfur absorption tests were performed in the TGA to compare the rate of reaction of zinc titanate sorbents as a function of temperature.

Figure 7 shows the TGA performance of MZT-R1 formulation in the range 371-482 °C (700-900 °F). After setting a baseline initial sample weight under simulated coal gases without H₂S, the H₂S was started at 30 minutes. The desulfurization rate of the sorbent results in a weight gain as the zinc component of zinc titanate goes from the oxide form to the sulfide form. A typical operating condition in a moving-bed reactor requires a sulfur loading 6.7 lb of sulfur/ft³ of bed. This target is shown as a horizontal line at the equivalent weight percentage versus time in Figure 7. For the chosen TGA test (at 1 atm, 3 % H₂S) to be a good predictor of sulfur loading in a moving-bed reactor, the target sulfur loading in the TGA must be accomplished in 2 hours of test time. It can be seen from Figure 7 that the sulfur loading at the TECo NOC (normal operating conditions) can be achieved with MZT-R1 by operation as low as approximately 700 °F. This performance suggests a window of about 200 °F below the NOC, albeit being considered off-design conditions. Currently other sorbent formulations are being evaluated for operation at temperatures below 900 °F.

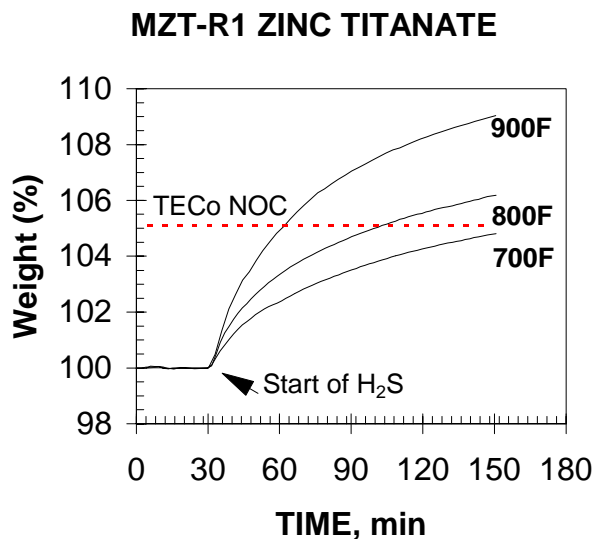


Figure 7. TGA reactivity of MZT-R1 zinc titanate as a function of temperature.

CRD bench reactor tests

Having evaluated TGA chemical reactivity and mechanical durability of small amounts of fresh pellets, five of the most promising formulations were selected for bench-scale screening at GE-CRD. The bench tests would provide information on the bed desulfurization performance and attrition resistance of the bed as a whole over multiple cycles of operation.

The bench screening was performed using a 7-cm (2.75 in.) ID fixed-bed bench reactor. Details of the bench reactor system and its operation have been given before [Ayala et al., 1994]. The cross sectional area of the reactor was divided into four quadrants, and each quadrant was filled with a different zinc titanate formulation. In this way, all four formulations were exposed for the same amount of time to the same flow rates, gas compositions, and initial temperatures during the test.

Target conditions for desulfurization bench tests that apply to any sorbent under development are summarized in Table 4. These bench test conditions are expected to translate into a steady state operation at normal operating conditions in the TECo moving-bed demonstration plant. The outlet H₂S at TECo is expected to be less than 50 ppmv at steady state.

Table 4.- Target test conditions during absorption in bench tests

<i>Parameter</i>	<i>Operating Condition</i>
Desired Sorbent Sulfur Loading	6-7 lb. S/ft ³ of bed (96.2 g S/liter of bed) at the gas inlet location
H ₂ S Breakthrough point	200 ppm
Gas space velocity	≥2000 hr ⁻¹ (STP)*
Pressure	20 atm
Temperature	482 °C (900 °F)

* STP (standard temperature and pressure) is defined at 20 °C and 1 atm.

Typical test conditions maintained during screening in the bench-scale reactor at CRD are presented in Table 5. At the end of the multiple cycles, typically five cycles of absorption and regeneration, the sorbent was removed from the reactor and the ASTM D-4058-81 attrition test performed on samples in each of the quadrants. By following this procedure, data can be collected on the composite desulfurization performance and individual mechanical durability of each of the sorbents.

Table 5. Test conditions for GE-CRD reactor system during quadrant bench tests

Test Gas Composition	Absorption	Reductive Regeneration	Oxidative Regeneration	Nitrogen Purge
CO	38.6	39.0		
CO ₂	5.7	5.7		
H ₂	34.7	35.1		
H ₂ O	20.0	20.2		
H ₂ S	1.0			
O ₂			2-5%	
SO ₂			8%	
N ₂			balance	
Pressure, atm	5 atm	5 atm	5 atm	1-5 atm
Sorbent Bed	900 °F	900 °F		
Temperature				
Space velocity (STP, 25 °C, 1 atm)	2000 h ⁻¹	2000 h ⁻¹	1000 h ⁻¹	750 h ⁻¹

The reactor size typically can accommodate up to 0.5 l of sorbent. In the so-called quadrant tests, the bed volume was adjusted to obtain the desired gas space velocity, meet the requirement of sulfur loading at the gas inlet location, meet the 200 ppmv breakthrough in a reasonable time (<5 hr.), and meet the current test schedule for screening. Test conditions during absorption (Table 5) followed the TECo guidelines for bench tests (Table 4), except for the reduced pressure (5 atm at CRD vs. 20 atm for preferred bench tests and 30 atm at TECo) and definition of breakthrough (200 ppmv in bench tests vs. less than 50 ppmv in the TECo plant). The chosen reduced pressure during absorption is a result of limitations in the existing GE-CRD bench hardware; a preferred condition for bench tests is 20 atm. The definition of breakthrough at 200

ppm rather than at 50 ppm was selected for ease of measurement and for historical comparisons. Regeneration was conducted at 5 atm and between 482 °C and 760 °C. The acceptable regeneration pressure range is 5 to 7 atm.

Figure 8 presents the composite H₂S breakthrough curves for four formulations in the quadrant bench test #1 (formulations MZT-I1, MZT-G1, MZT-O1, and MZT-R1). This test consisted of loading the bench reactor with four different formulations arranged in quadrants, so that each of them was exposed for the same time to the same base temperature and gas compositions. The only potential difference in test conditions is that each sorbent may exhibit a different temperature rise during regeneration, which would be characteristic to each sorbent; however, the exposure time was the same for all four sorbents in both absorption and regeneration modes.

For comparison purposes and to show the relative performance of the modified zinc titanates with respect to prior baseline zinc titanate sorbents, Figure 9 shows the performance of the same T-2594M zinc titanate under similar bench tests when 8%SO₂ was present in the regeneration gas from the very first cycle. Note the difference in breakthrough sulfur capacity between the results for T-2594M in Figure 9 and the modified zinc titanates in Figure 8. Figure 10 shows the corresponding performance of the same T-2594M in the GE pilot plant Test #8 (September 1995) when the sorbent desulfurization performance (99% sulfur removal) was satisfactory in both in the bench tests and in the actual GE pilot plant operation.

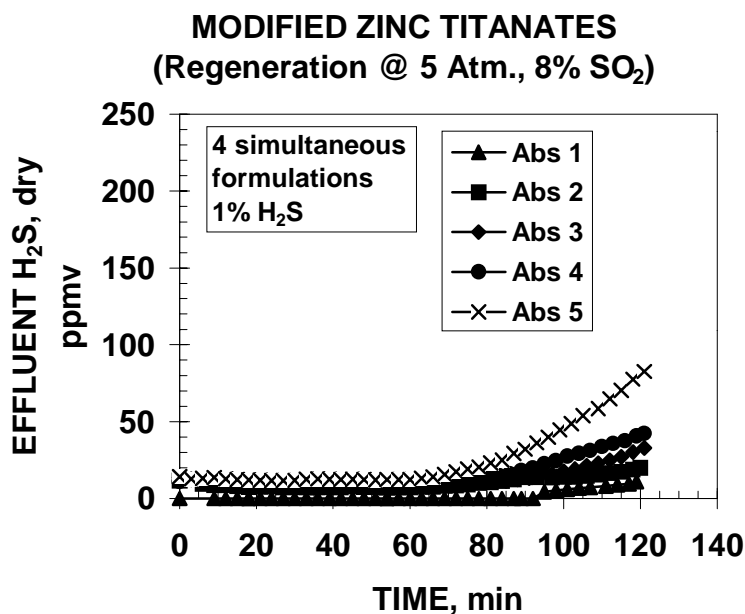


Figure 8. Breakthrough curves during absorption for the modified zinc titanate sorbents (Quadrant Bench Test #1)

Since T-2594M had satisfactory desulfurization in the pilot plant absorber (99% desulfurization efficiency, Figure 10), we can expect improved performance of the modified zinc titanates over T-2594M in pilot plant tests.

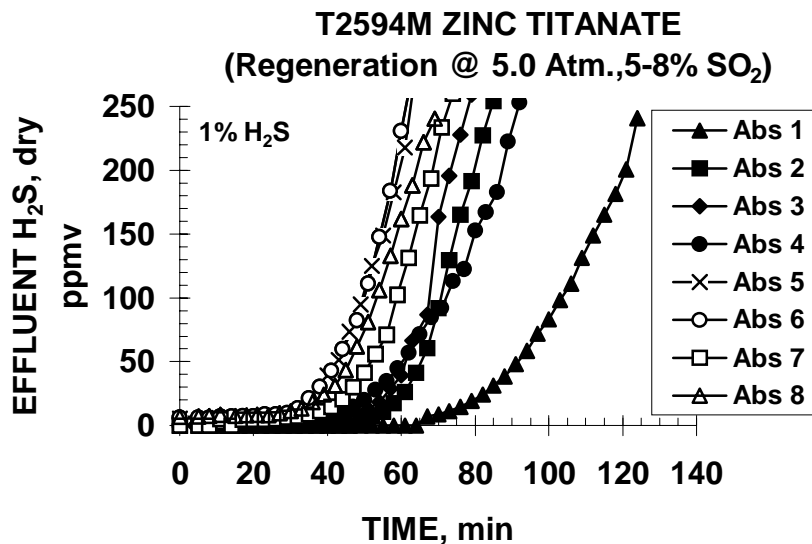


Figure 9. Breakthrough curves for T-2594M zinc titanate with regeneration at 5 atm and 8% SO₂ present in the regeneration gas

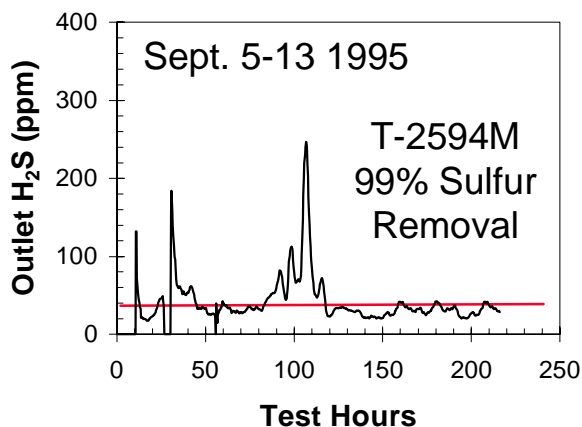


Figure 10. Outlet H₂S concentration from the pilot plant absorber using T-2594M during Test 8 (1995)

Mechanical durability of cycled formulations

Figure 11 presents the results of attrition ratios for the four formulations tested in the Quadrant Bench Test #1 (formulations MZT-I1, MZT-G1, MZT-O1, and MZT-R1). The attrition ratio is defined as the percent ASTM attrition loss in the final state (5th regeneration) divided by the

ASTM percent attrition loss in the fresh state. Samples were taken from the gas inlet location, where the highest sulfidation and regeneration levels are experienced by the sorbent. In addition, the corresponding attrition ratio for the baseline T-2594M is presented also. The attrition ratio was used in the chart to highlight the relative degradation of the pellets. For instance, an attrition ratio of 1.0 means that there was no degradation in the sorbent over the test duration. An attrition ratio less than 1 means that the sorbent became stronger in its final state while an attrition ratio greater than 1 means that the sorbent experienced a degradation in (i.e., weakening). The absolute values of the ASTM attrition losses were in the range 1 to 2%.

The best two formulations, MZT-R1 and MZT-I1 are being considered for testing in 25-cycle bench tests at RTI as part of the qualification of sorbents for Teco's 2nd sorbent fill. There are other formulations that will be tested at GE as part of the Quadrant Bench Test #2 in the future.

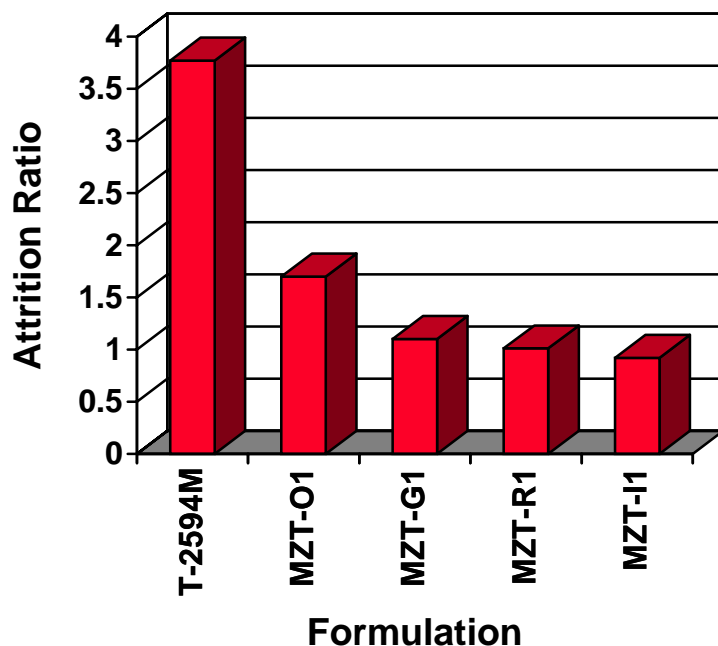


Figure 11. Attrition resistance ratios of zinc titanate formulations after 5 cycles of bench-scale testing (Quadrant Bench Test #1)

RTI's Independent Bench Evaluation

Given the satisfactory performance of two of the modified zinc titanate formulations MZT-R1 and MZT-I1 during the screening process at GE-CRD, one of them will be recommended for independent bench testing at Research Triangle Institute (RTI) through 25-cycles of bench testing under a separate DOE-sponsored program.

To date, MZT-R1 has undergone a preliminary 5-cycle screening test at RTI to check various operating conditions for the future long-term testing. Figure 12 presents the H₂S breakthrough curves during absorption at 20 atm. These curves are comparable to those obtained at GE-CRD at

5-atm absorption during preliminary multiple cycle tests where MZT-R1 was included. Table 6 presents the current accomplishments during the bench screening at RTI. Most objectives were achieved at 5 cycles, but corroboration after 25 cycles is still needed for the ASTM attrition test. In view of the results obtained thus far, it appears that the modified zinc titanate formulations MZT-R1 and MZT-II are potential candidates for meeting both the chemical reactivity and mechanical durability required of a sorbent for operation as a second fill at Teco's Polk Station hot gas cleanup system.

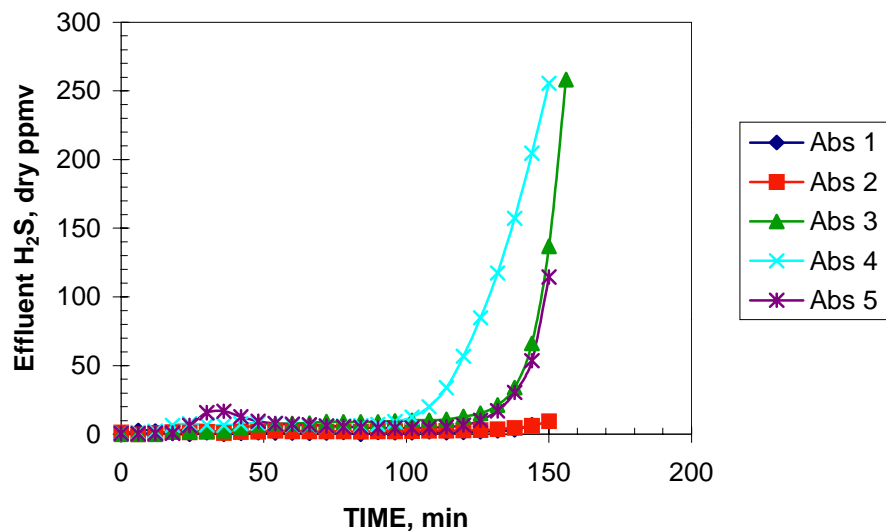


Figure 12. Breakthrough curves for MZT-R1 sorbent for 5-cycles in screening bench tests performed at RTI.

Table 6. Current results of screening tests at RTI on MZT-R1

Parameter	25-Cycle Bench Test Targets	Results after 5 cycles
Absorption Temperature	482 °C (900 °F)	482 °C (900 °F)
Base Regeneration Temp.	343-538 °C (650-1000 °F)	482 °C (900 °F)
Reg. Pressure	5-7 atm	5 atm
Fresh ASTM attrition loss	<4%	2%
25-cycle ASTM attrition loss	<5%	N/A
Net Sulfur Loading	> 0.11 g S/cc bed (6.7 lb. S/ft ³ bed)	0.11 g S/cc bed (6.7 lb. S/ft ³ bed)*

Benefits

Coal gas desulfurization to sufficiently low levels at elevated temperatures is now recognized as crucial to efficient and economic coal utilization in Integrated Gasification-Combined Cycle (IGCC) systems. Sensitivity studies of IGCC systems in The Netherlands [Schreurs, 1994; Droog et al., 1993] outlined the economic advantages of desulfurization at 350 °C or above over commercial low-temperature cleanup systems below 100 °C, while in the U.S. an independent study [Buchanan et al., 1994] compared different configurations of gasifiers, hot gas desulfurization (including moving-bed systems), particulate cleanup, and process integration to compare the performance of several system configurations. In both cases, the assumptions for successful implementation of hot coal gas desulfurization relied on the successful development of regenerable sorbent materials.

These sorbents must meet a minimum set of chemical reactivity and mechanical durability criteria to reduce operating costs in large systems. The present sorbent development program is aimed at minimizing the risks (technical and cost) associated with scaling up of the moving-bed hot gas desulfurization process.

Over the past few years, testing of zinc titanate sorbent in laboratory screening, long-term bench scale testing, and pilot plant scale operation, has proven that zinc titanate is a suitable sorbent for desulfurization in the target temperature range of 343-538 °C, and consistent with relatively easy regeneration requirements and minimal undesired side reactions. In this sense, the advanced sorbent development program is providing support to the development of more efficient and economically viable large-scale IGCC systems for power generation.

Future Activities

Having demonstrated that modified zinc titanate sorbents can achieve 99% desulfurization simultaneously with easy sorbent regeneration and mechanical durability, the next step is to further prove improvements the mechanical durability of the sorbent over the extended 25-cycle tests at RTI. Evaluation and data analysis of other sorbents fabricated by different manufacturers will be conducted in conjunction with TECo and the U.S. DOE. The outcome of the selection process will be a robust formulation for consideration as a second sorbent fill in the demonstration of HGCU technology under the Clean Coal Technology Program at the TECo Polk Station.

Acknowledgments

The authors gratefully acknowledge the technical assistance of Daniel Cicero, P.E., the DOE Contracting Officer's Representative, and R.P. Gupta and B. Turk for the performance of the independent testing at RTI under DOE sponsorship. United Catalysts, Inc.'s participation is also appreciated for helpful discussions and for providing several sorbent formulations for testing. Participation of Chemetals, Inc., and E&A Associates as sorbent providers to this program is

also appreciated. The contract period of performance is from September 30, 1994 to February 29, 1997.

References

- Abbasian, J., R.B. Slimane, J.R., Wangerow, and M.K. Zarnegar. 1997. Advanced Low Temperature Sorbents for Fluid-Bed Applications. In *Proceedings of the Advanced Coal-Based Power and Environmental Systems '97 Conference*. Pittsburgh, PA. July 22-24, 1997. Sponsored by U.S. Dept. of Energy/Federal Energy Research Center.
- Ayala, R.E. and T.L. Chuck, 1997. 1996 Annual Technical Report for the Advanced Sorbent Development Program. DOE Contract No. DE-AC21-MC9431089. January 1997.
- Ayala, R.E. T.L. Chuck, and R.P. Gupta. 1996. . Moving-Bed Sorbents. In *Proceedings of the Advanced Coal-Fired Power Systems '96 Review Meeting*, July 16-18, 1996. CD ROM. Morgantown Energy Technology Center.
- Ayala, R.E. and T.L. Chuck, 1996. Final Report. Enhanced Durability of High-Temperature Desulfurization Sorbents for Moving-Bed Applications. DOE Contract No. DE-AC21-88MC25003. May 1996.
- Ayala, R.E. T.L. Chuck, and R.P. Gupta. 1995a. . Moving-Bed Sorbents. In *Proceedings of the Advanced Coal-Fired Power Systems '95 Review Meeting*, Vol II , pp 591-600. DOE/METC-95/1018 Vol 2. NTIS/DE95009733. Springfield, Va.: National Technical Information Service.
- Ayala, R.E., V.S. Venkataramani, J. Abbasian, and A.H. Hill. 1995b. Advanced Low-Temperature Sorbents. In *Proceedings of the Advanced Coal-Fired Power Systems '95 Review Meeting*, Vol I , pp 407-416. DOE/METC-95/1018 Vol. 1. NTIS/DE95009732. Springfield, Va.: National Technical Information Service.
- Ayala, T. Chuck, E. Gal, and R.P. Gupta. 1994. Development of High Temperature Desulfurization Sorbents for Moving-Bed Systems. In *Proceedings of the Coal-Fired Power Systems 94 – Advances in IGCC and PFBC Review Meeting*, p. 637. DOE/METC-94/1008. NTIS/DE94012252. Springfield, Va.: National Technical Information Service.
- Bevan, D.J. Najewicz, R.E. Ayala, A. Feitelberg, and A. Furman. 1995. Integrated Operation of a Pressurized Gasifier, Hot Gas Desulfurization System and Turbine Simulator. In *Proceedings of the Advanced Coal-Fired Power Systems '95 Review Meeting*, Vol I , pp. 187-201. DOE/METC-95/1018. NTIS/DE95009732. Springfield, Va.: National Technical Information Service.
- Buchanan, T.L., H.T. Chen, M.G. Klett, M.D. Rutkowski, and R. Zaharchuk. Optimization of Stream Cleanup in Three IGCC Systems. Final Report to U.S. DOE/Fossil Energy by Gilbert/Commonwealth, Inc., Reading, PA, USA under Contract DE-AC01-88FE61660.

- Corman, J.C. 1986. *System Analysis of Simplified IGCC Plants*, Topical Report. U.S. Dept of Energy, DOE/ET/14928-2233.
- Droog, H.A., A. Delwel, and R. Assink. 1993. Comparison of High-Temperature Gas Treatment Options with Low-Temperature Gas Treatment in IGCC's following Entrained Flow Gasification. In *Proceedings 12th EPRI Conference on Gasification Power Plants*. San Francisco, CA, Oct 27-29, 1993
- Furman, A.H., R. Ayala, A. Feitelberg, D. Najewicz. 1996. Integrated Operation of a Pressurized Fixed Bed Gasifier, Hot Gas Desulfurization System and Turbine Simulator. Paper 3.1. *Advanced Coal-Fired Power Systems '96 Review Meeting*. Morgantown, WV, July 16-18, 1996.
- Swisher, J., 1997. Highly Attrition Resistant Moving-Bed Zinc Titanate Sorbent. Advanced Coal-Based Power and Environmental Systems '97 Conference. U.S. Dept. of Energy/Federal Energy Technology Center. Pittsburgh, PA, July 22-24, 1997.
- Rath, L.K., G.T. Lee, and P.H. Le. 1994. IGCC System Studies. In *Proceedings of the Coal-Fired Power Systems 94 – Advances in IGCC and PFBC Review Meeting*, p. 66. DOE/METC-94/1008. NTIS/DE94012252. Springfield, Va.: National Technical Information Service.
- Schreurs, H. 1994. Hot Clean Up of coal Gas. An Overview of Applicability. Netherlands Agency for Energy and the Environment Novem. August 31, 1994. Report No. 94/E0705/229100.